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Optical absorption studies on ferrous ion doped CMDH crystals

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Abstract : The optical absorption spectra of ferrous ion doped cadmium maleate dihydrate (CMDH) are studied at room and liquid nitrogen temperatures. The spectra are characteristic of Fe^{2+} in CMDH in a distorted octahedral symmetry. Only broadening without any splitting of the spin-allowed band indicates trigonal distortion associated with Jahn-Teller effect. Crystal field parameters are evaluated.

Keywords : Optical absorption spectra, ferrous ion, CMDH

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The present article deals with the optical absorption spectra of ferrous ion doped cadmium maleate dihydrate (CMDH) crystals. CMDH is monoclinic with space group $P\,2_1/C$ and has eight molecules per unit cell [1]. It contains two crystallograhically and chemically distinct Cd atoms. One of them Cd (1) is surrounded by six oxygen atoms, four of which are from water molecules and the other two are from carboxyl groups. The other atom Cd (2) is eight-coordinated with distorted dodecahedral geometry, through four chelated carboxyl groups from the maleate ligands. Therefore, any transition metal ion may enter substitutionally into the Cd (1) or Cd (2) site or may enter into any interstitial site.

From the results of EPR investigations on VO^{2+} and Cu^{2+} doped CMDH, the substitutional replacement of transition metal ion was ruled out and interstitial entry was proposed [2]. The authors investigated earlier the optical absorption spectra of Mn^{2+}, Co^{2+} and Ni^{2+} in the host CMDH. The Co^{2+} doped CMDH spectrum is characteristic of d^7 in O_h symmetry [3]. The Ni^{2+} and Mn^{2+} doped CMDH exhibit octahedral symmetry with trigonal distortion [3,4]. The present investigation is to ascertain the site symmetry of the ferrous ion in the host CMDH.

Cadmium maleate dihydrate (CMDH) crystals are grown at room temperature by slow evaporation of the solution prepared by addition of an aqueous solution of maleic acid

to an excess of cadmium carbonate in water followed by heating to near boiling point. To grow the Fe^{2+} doped crystals, a few drops of the aqueous solution of ferrous sulphate are added to the resultant solution. The growth solution is cooled, filtered and allowed to evaporate at room temperature. Good transparent crystals are grown in about a fortnight.

The optical absorption spectra are recorded on Hitachi-U 3400 spectrophotometer in the region 300–1300 nm both at room and liquid nitrogen temperatures.

For Fe^{2+} ion ($3d^6$), the free ion terms are ^5D, ^3H, ^3P, ^3F, ^3G, ^3D, ^1I and ^1D of which ^5D is the ground state term. In an octaherdal field, the ^5D term splits into ^5E_g and $^5T_{2g}$ levels with $^5T_{2g}$ as the ground state. Accordingly, only one spin-allowed transitin $^5T_{2g} \rightarrow {}^5E_g$ exists Due to Jahn-Teller effect, the corresponding band either broadens or splits into two components depending upon the nature of the descent in symmetry. The average of these two components is a measure of 10 Dq band in case of the splitting of the band. Other bands are spin-forbidden and are weaker [5].

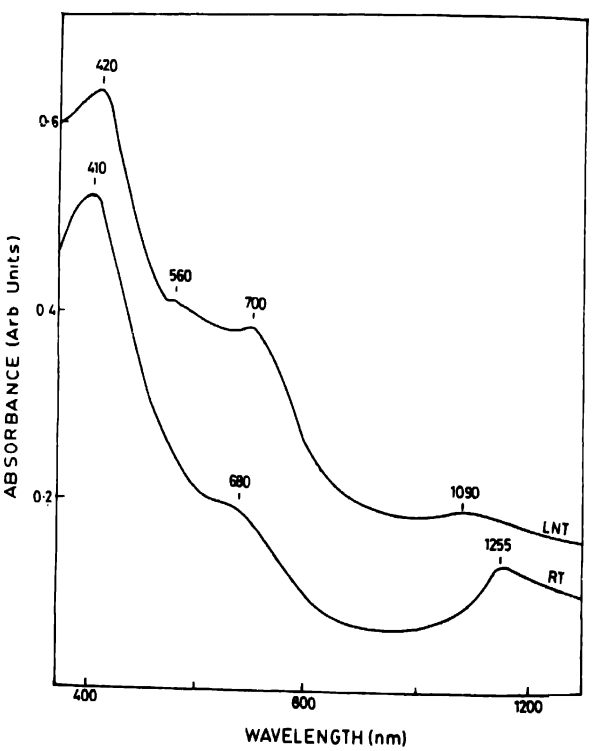

Figure 1. Optical absorption spectra of ferrous ion doped CMDH in the region 300–1300 nm

The optical absorption spectrum at the room temperature (RT) exhibits three bands 1255, 680 and 410 nm. In the spectrum at liquid nitrogen temperature (LNT), the three

bands are shifted and are observed at 1090, 700 and 420 nm respectively. In addition, another weak band is observed at 560 nm. Optical absorption spectra of the ferrous ion doped CMDH are shown in Figure 1.

The bands are characteristic of ferrous ion in the host CMDH. In the spectrum at RT, the intense broad band observed at 1090 nm is attributed to the spin-allowed transition $^5T_{2g}(D) \rightarrow {}^5E_g(D)$. The weak bands at 560, 700 and 420 nm are attributed to the transitions $^5T_{2g}(D) \rightarrow {}^3T_{2g}(H)$, $^5T_{2g}(D) \rightarrow {}^3T_{1g}(H)$ and $^5T_{2g}(D) \rightarrow {}^1T_{1g}(I)$ respectively. The band corresponding to the transition $^5T_{2g}(D) \rightarrow {}^5E_g(D)$, shifts to shorter wavelength side at LNT and this is in accordance with the positive slope of the corresponding $^5E_g(D)$ term in the Tanabe-Sugano diagram [6]. Other bands are shifted towards longer wavelength side at LNT. These shifts are also in accordance with the negative slopes of the corresponding terms in the Tanabe-Sugano diagram. These observations confirm the assignment of the bands. By solving the energy matrices of d^6 configuration, the following crystal field (Dq) and interelectronic repulsion (B and C) parameters are evaluated : $Dq = 920$; $B = 950$ and $C = 4250$ cm^{-1}. The observed band-head data along with the calculated values is given in Table 1.

Table 1. Band-head data along with the calculated values of ferrous ion doped CMDH

Transitions from $^5T_{2g}(D)$	Band positions				
	observed				calculated
	RT		LNT		
	λ (nm)	ν (cm^{-1})	λ (nm)	ν (cm^{-1})	ν (cm^{-1})
$^5E_g(D)$	1255	7966	1090	9172	9200
$^3T_{1g}(H)$	680	14702	700	14282	14272
$^3T_{2g}(H)$	-	-	560	17852	17841
$^1T_{1g}(I)$	410	24383	420	23803	23764

The $^5E_g(D)$ state is subjected to the strong influence of the Jahn-Teller effect, that causes the splitting of ^5E_g term due to the inner configuration instability of this state. This results in splitting of the bands in tetragonal and rhombic symmetries. In trigonal distortion, it does not result in splitting though it results in broadening of the band thus confirming the trigonal symmetry.

To conclude, the present investigation reveals that the spectrum of Fe^{2+} doped CMDH is characteristic of six coordinated Fe^{2+} with trigonal distortion. Therefore, the interstitial site of the transition metal ion in CMDH is ascertained to possesses trigonally distorted octahedral symmetry.

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